ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

Funded by
the European Union

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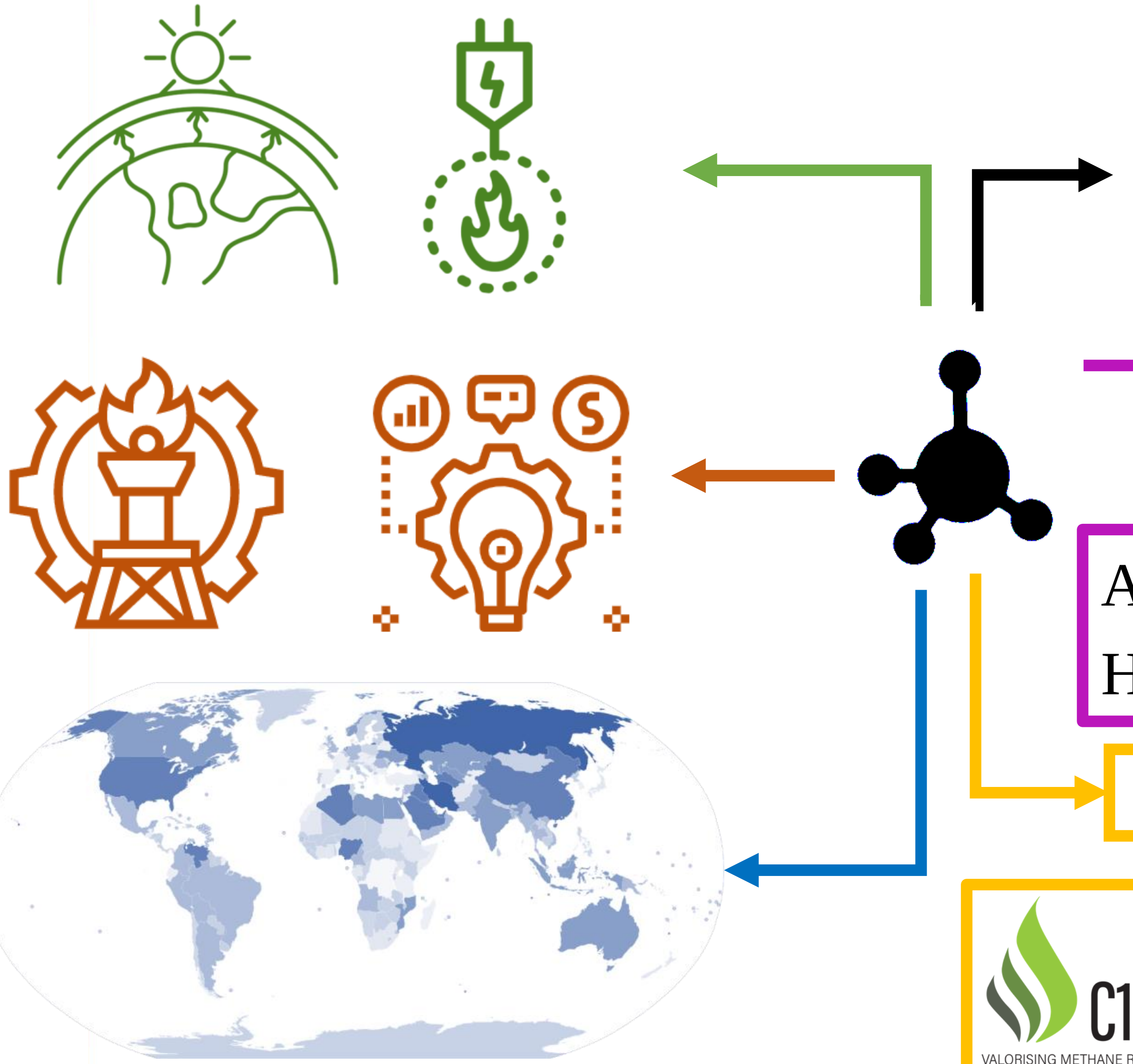
Catalysts and processes for the conversion of methane to CO and ethylene

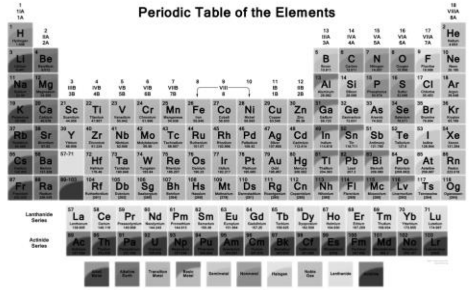
Alejandro Romero Limones

Methane valorization



OCM

$CH_4 \rightarrow C_2$



MEMERE · ADREM Adaptable Reactors for Resource- and Energy-Efficient Methane Valorisation · ocmol Taking advantage of resources

Aiming at high C_2H_4 yields

High energy-intensive separation C_2H_4/C_2H_6

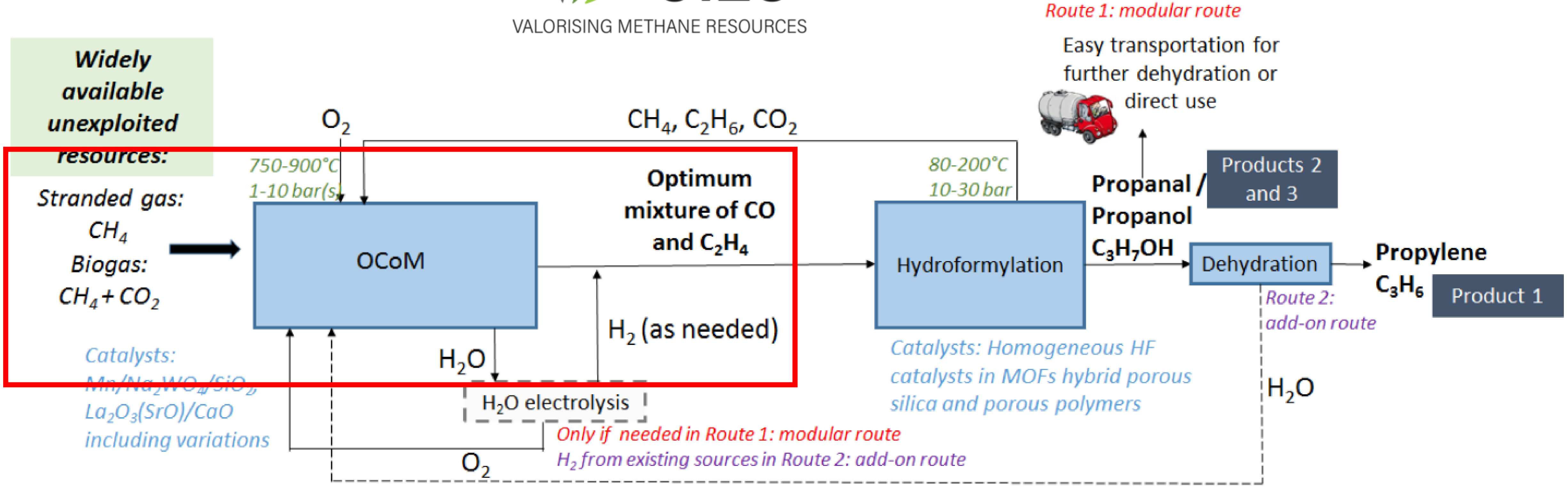
Side reactions exploitation $CH_4 \rightarrow C_2H_4 : CO$

C123 VALORISING METHANE RESOURCES

What if cheap methane sources could bring high-value C_3 products while largely reducing their carbon footprint?

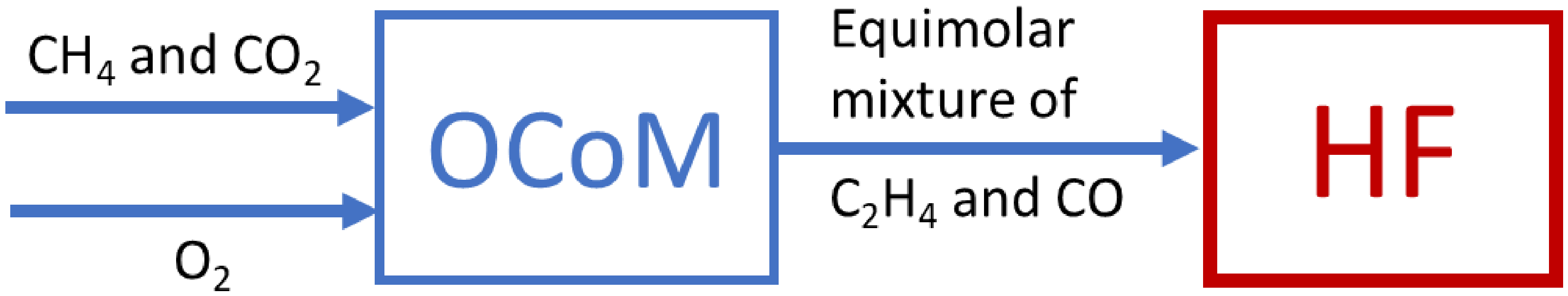
Outline

- C123 overview
- Catalyst candidates for OCoM
- Kinetic modelling
- OCoM process
- Conclusion and future work



$$CH_4 \longrightarrow C_2H_4 + CO \longrightarrow C_3$$

Oxidative Conversion of Methane



OCM Catalysts candidates

- La-Sr/CaO
- $MnNaW/SiO_2$
- $MnNaW/Al_2O_3$
- Al_2O_3

Identify the most suitable catalyst

Operating conditions

- $p_T < 6$ bar
- T = 750 – 1000 °C
- $CO_{2,in} < 20$ %
- $2 < CH_4/O_2 < 10$

Determine optimal operating conditions

Kinetic modeling

- OCM
- Thermal Dehydrogenation of Ethane

In-house developed. Parameters from literature

OCoM

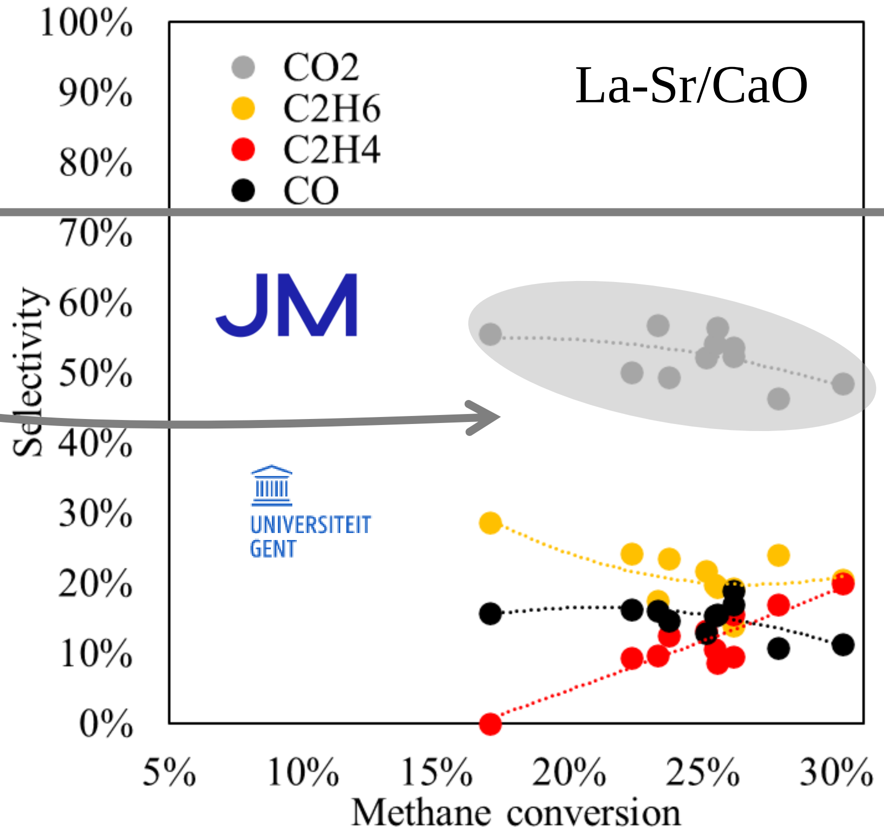
- OCoM reactor
- Post-Bed Cracking

Real scenario evaluation

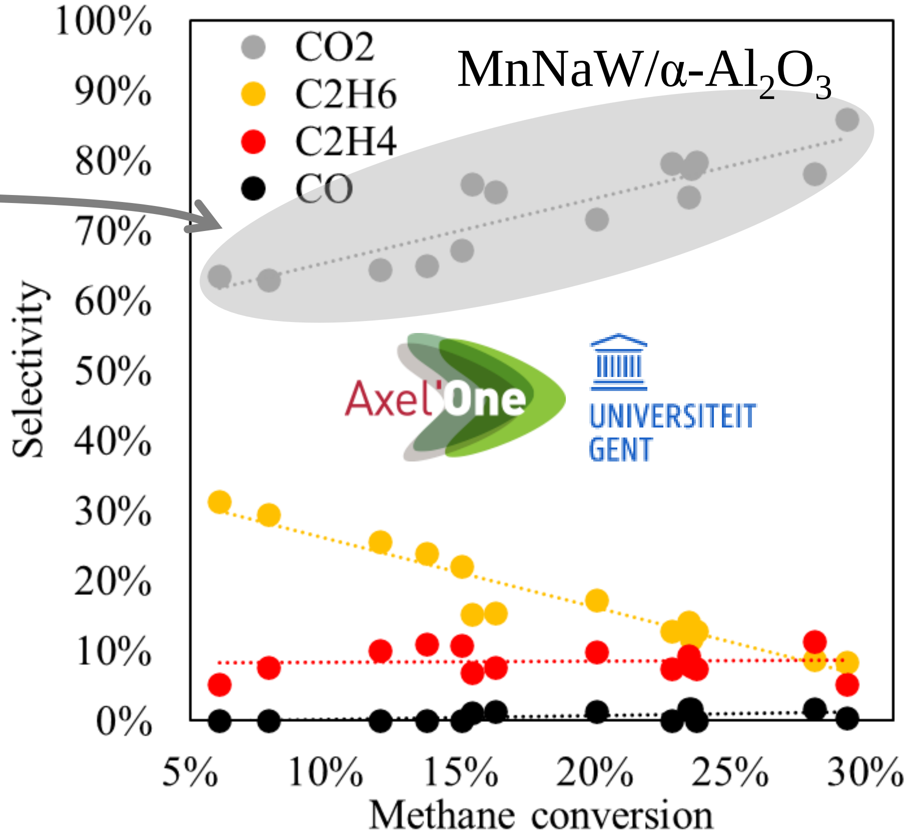
EU-project Horizon 2020 GA No. 814557 C123 Methane oxidative conversion and hydroformylation to propylene

Catalyst performance tests

Excess of CO_2



T = 800 °C; p_T = 1 bar;
W/F_{CH4} = 0.8 – 2.5 kg s mol^{-1}



T = 750 – 850 °C; p_T = 1 – 2 bar;
W/F_{CH4} = 1 – 4 kg s mol^{-1}

$$X_C = \frac{F_{C,0} - F_C}{F_{C,0}}$$

$$S_i = \frac{C_i\left(F_i - F_{i,0}\right)}{\sum_{j=1}^{n} C_j\left(F_j\right) - F_{CO_2,0}}$$

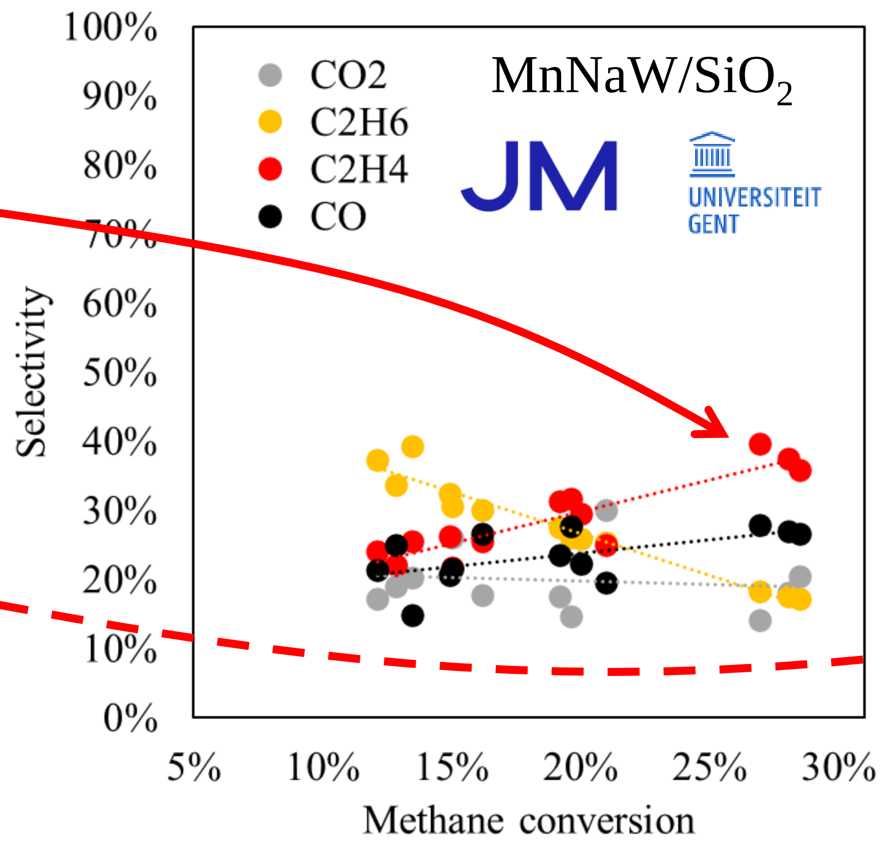
Best performance

S_{C2H4} ~ 40%
X_{CH4} ~ 30%

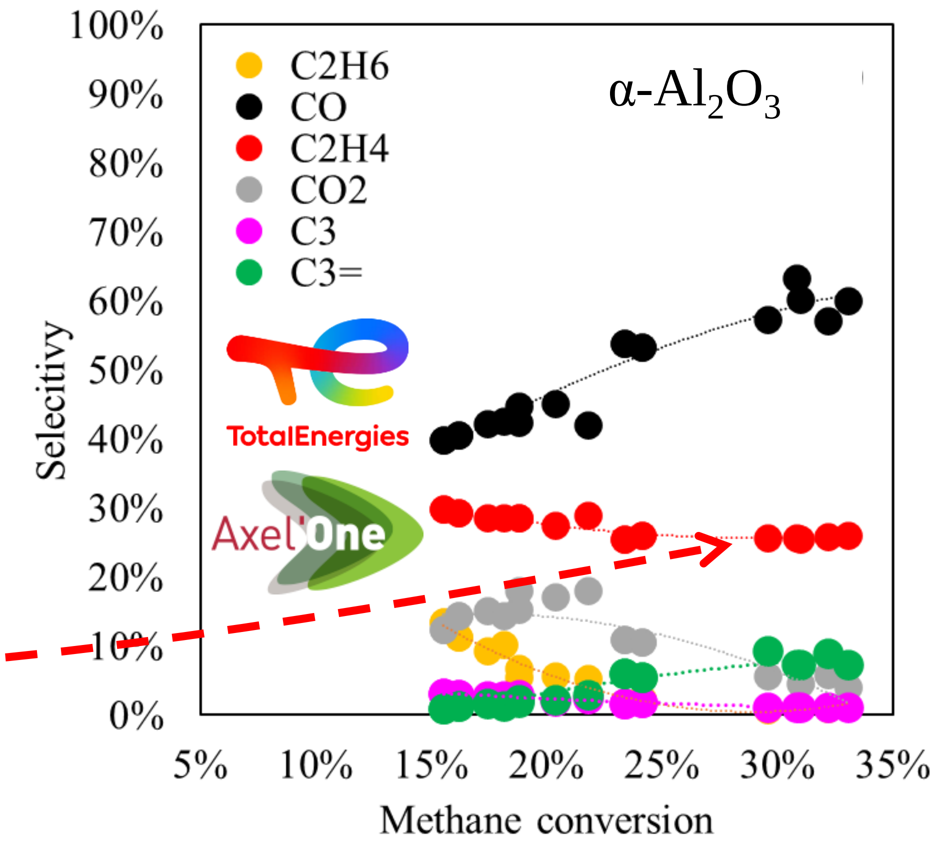
S_{C2H4} ~ 30%
X_{CH4} ~ 30%

$$X_C = \frac{F_{C,0} - F_C}{F_{C,0}}$$

$$S_i = \frac{C_i\left(F_i - F_{i,0}\right)}{\sum_{j=1}^{n} C_j\left(F_j\right) - F_{CO_2,0}}$$

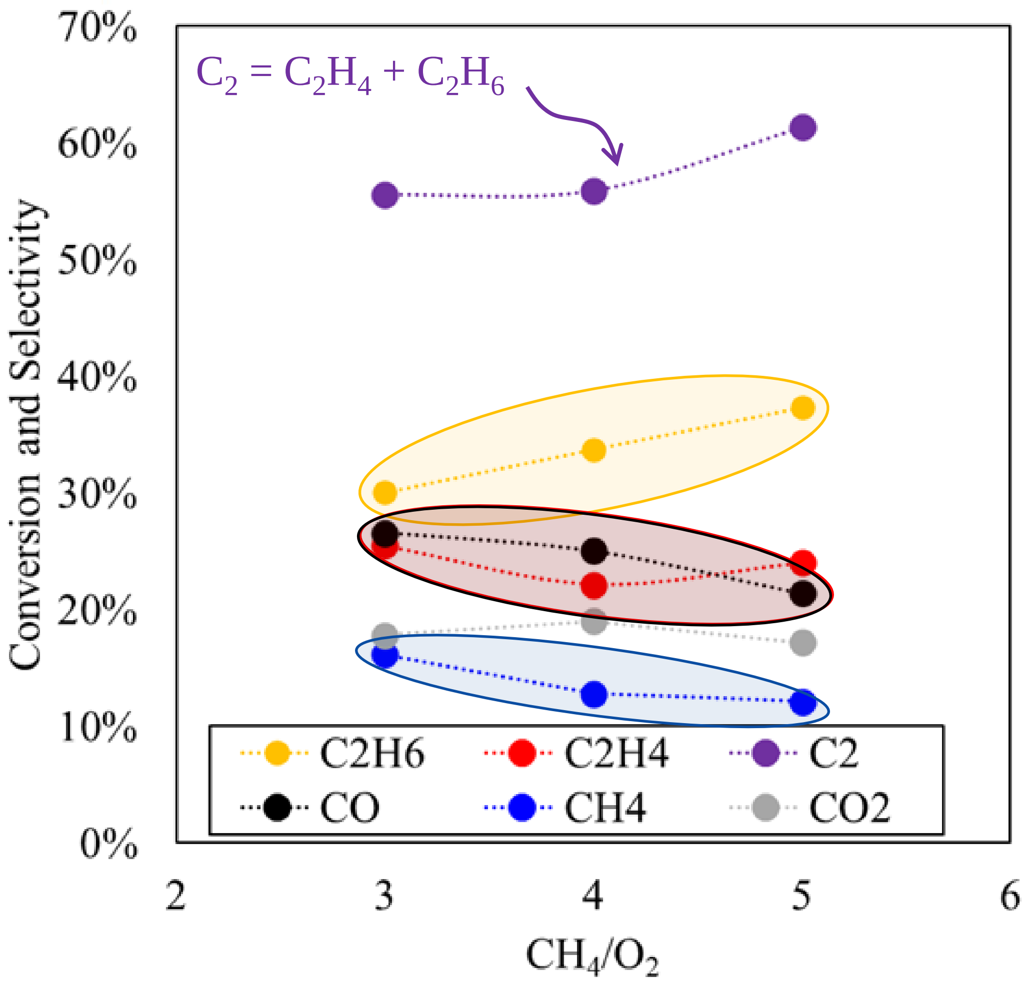


T = 800 – 850 °C; p_T = 1 bar;
W/F_{CH4} = 2 – 2.5 kg s mol^{-1}



T = 950 – 1000 °C; p_T = 1 – 3 bar;
W/F_{CH4} = 27.5 – 68.7 kg s mol^{-1}

From OCM to OCoM: Impact of CH_4/O_2

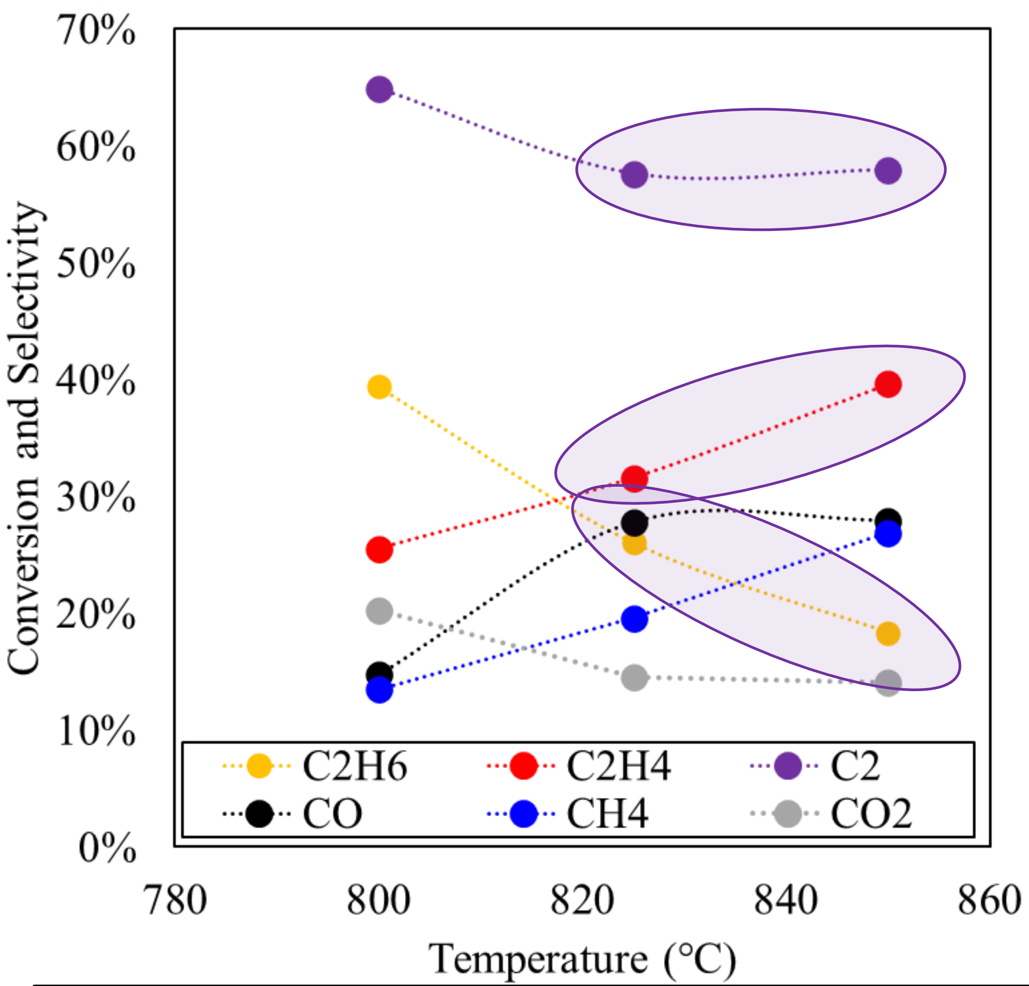


T = 800 °C; p_T = 1 bar; W/F_{CH4} = 2.5 kg s mol^{-1}

Acronym	Reaction steps
OCM	$CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O$
TOM	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
POM	$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$
ODH	$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$
POEt	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$

5 oxidation reactions are proposed based on experimental measurements

From OCM to OCoM: Impact of temperature

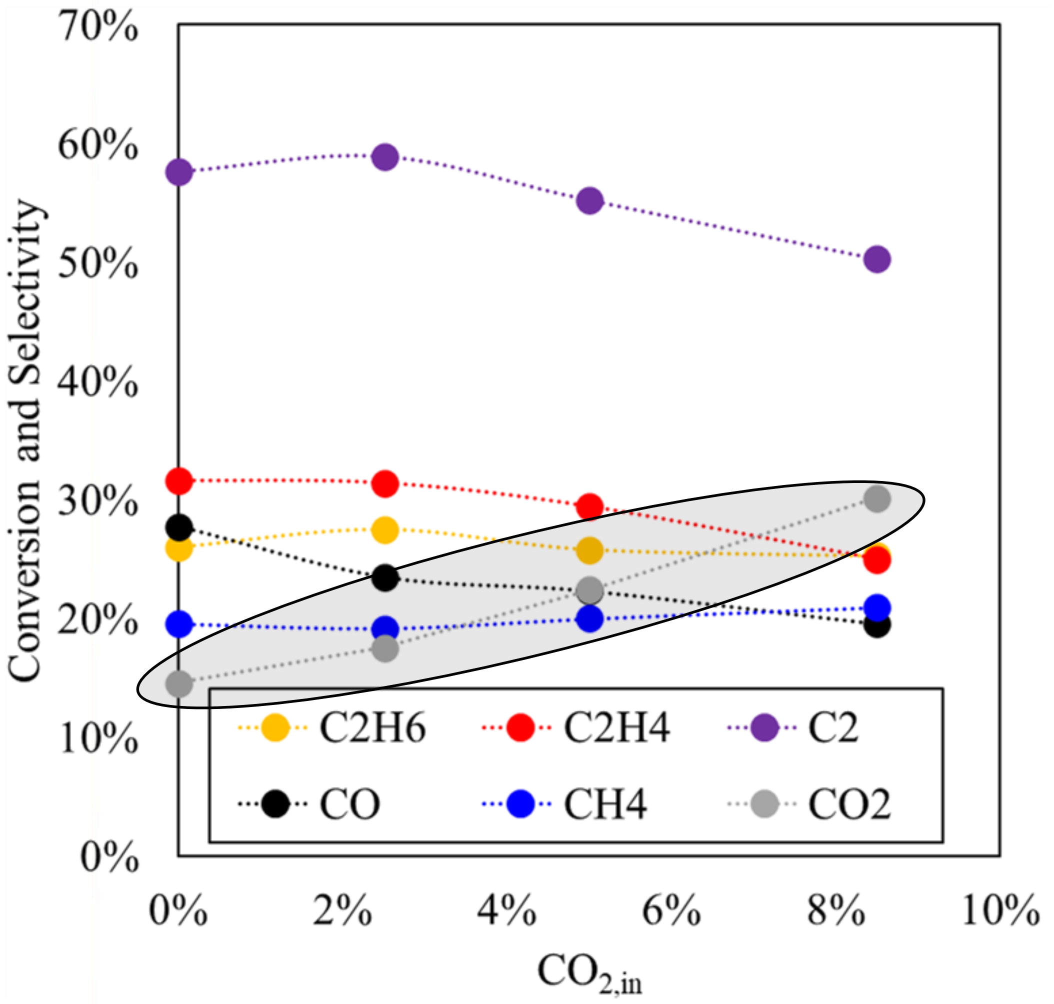


$CH_4/O_2 = 4$; $p_T = 1$ bar; $W/F_{CH4} = 2.5$ kg s mol^{-1}

Acronym	Reaction steps
OCM	$CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O$
TOM	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
POM	$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$
ODH	$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$
POEt	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$
TDE	$C_2H_6 \rightarrow C_2H_4 + H_2$

The thermal dehydrogenation is proposed based on the increase in S_{C2H4} while S_{C2} remains the same

From OCM to OCoM: Impact of CO_2



T = 800 °C; CH_4/O_2 = 4, 1 bar; W/F_{CH4} = 2.5 kg s mol^{-1}

Acronym	Reaction steps
OCM	$CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O$
TOM	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
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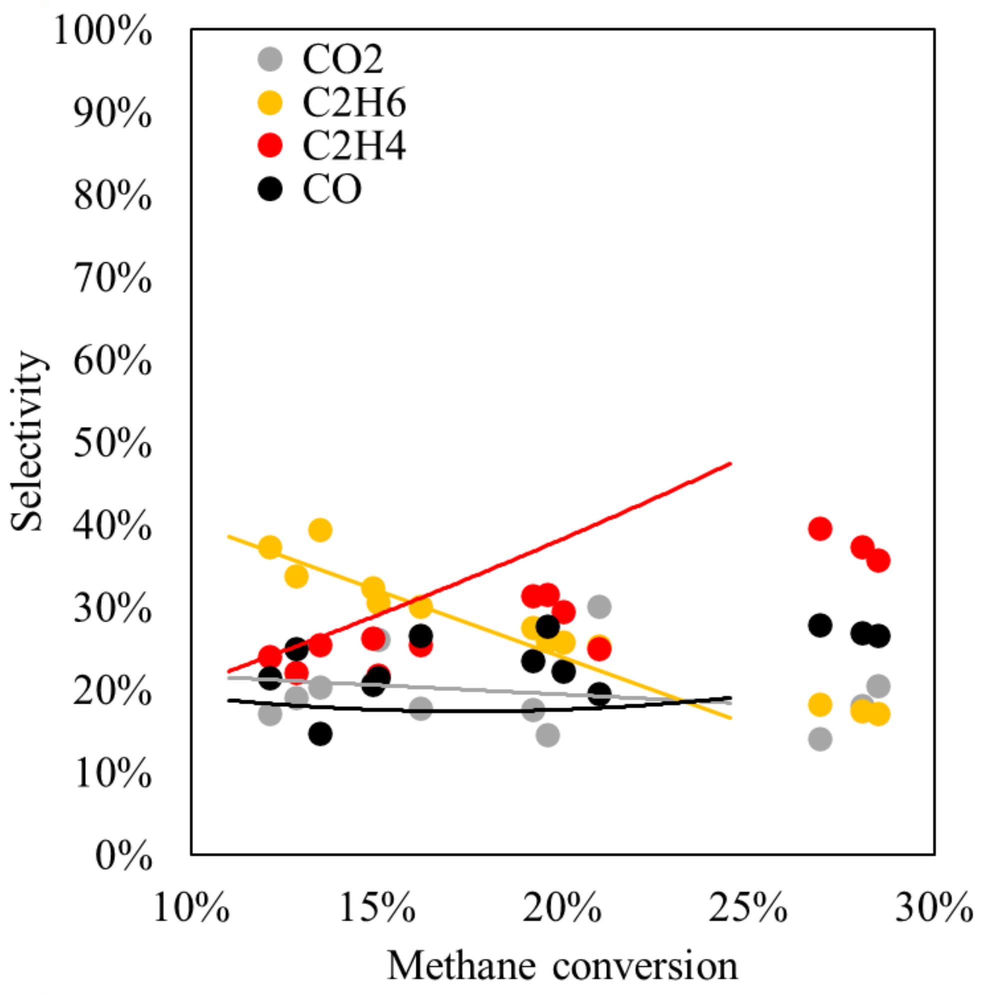
POEt	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$
TDE	$C_2H_6 \rightarrow C_2H_4 + H_2$

CO_2 has no effect on methane conversion, but decreases the selectivity towards the other compounds

$$S_i = \frac{C_i(F_i - F_{i,0})}{\sum_{j=1}^{n} C_j(F_j) - F_{CO_2,0}}$$

Kinetic model description



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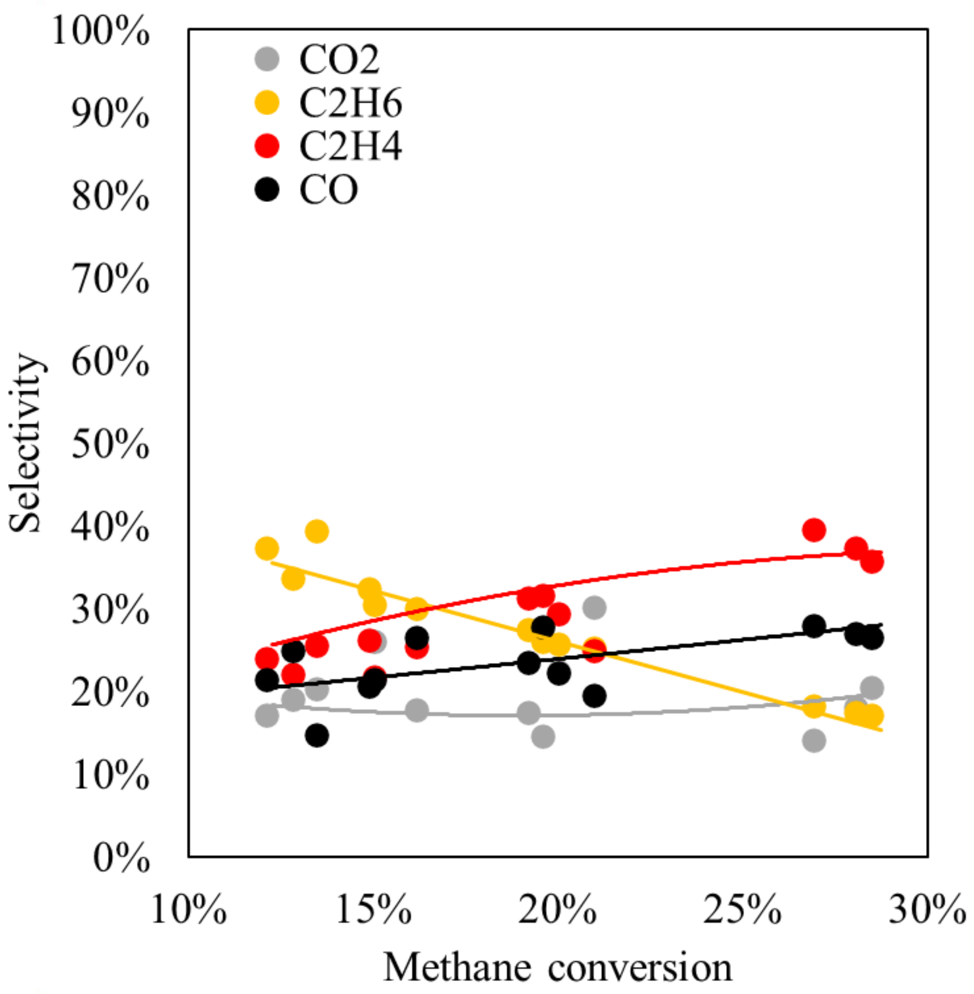
POEt	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$
TDE	$C_2H_6 \rightarrow C_2H_4 + H_2$
WGSR	$CO + H_2O \rightarrow CO_2 + H_2$

The 7 reaction steps that explain experimental observations do not allow description of experimental selectivities and methane conversion

Adding Steam Reforming of Methane into the kinetic model



Acronym	Reaction steps
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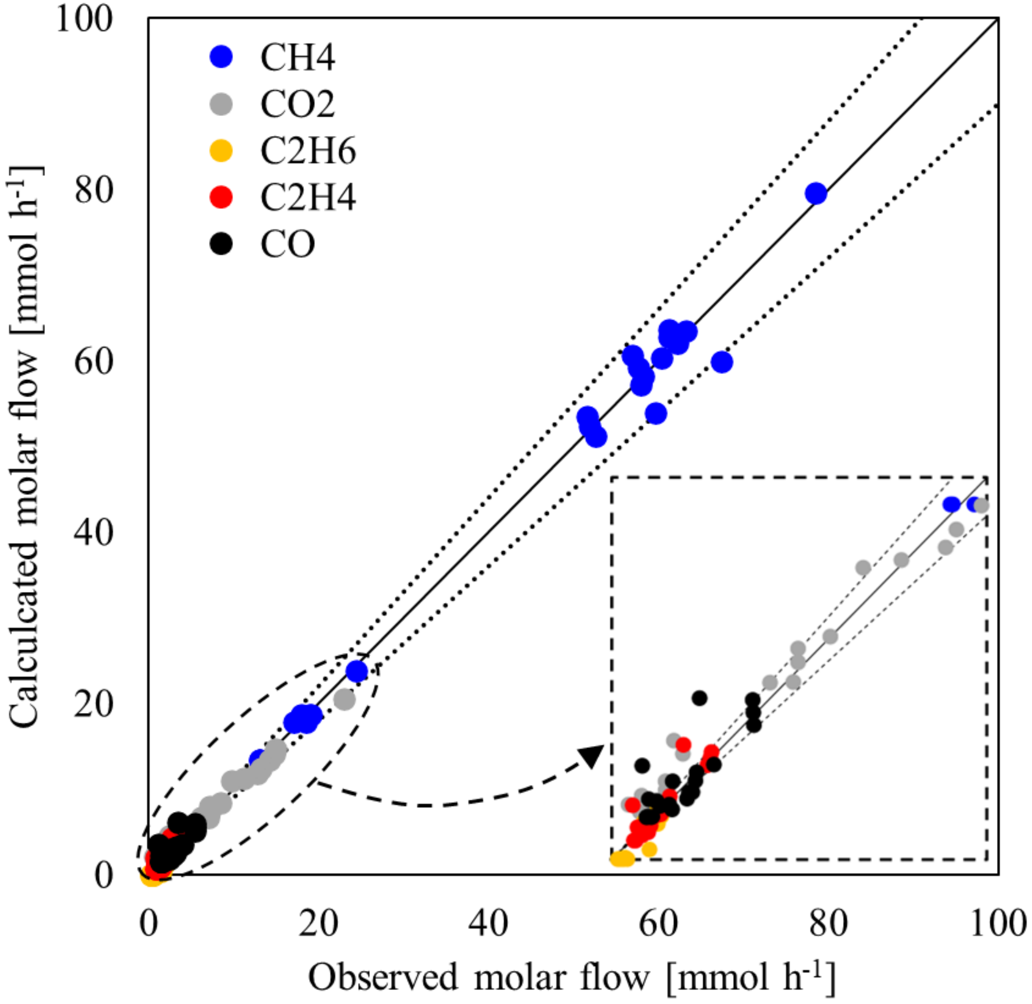
TOM	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
POM	$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$
ODH	$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$
POEt	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$
TDE	$C_2H_6 \rightarrow C_2H_4 + H_2$
WGSR	$CO + H_2O \rightarrow CO_2 + H_2$
SRM	$CH_4 + H_2O \rightarrow CO + 3H_2$

Addition of Steam Reforming of Methane allows quantitative description of selectivities and methane conversion

Parity plot



Acronym	Reaction steps
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SRM	$CH_4 + H_2O \rightarrow CO + 3H_2$

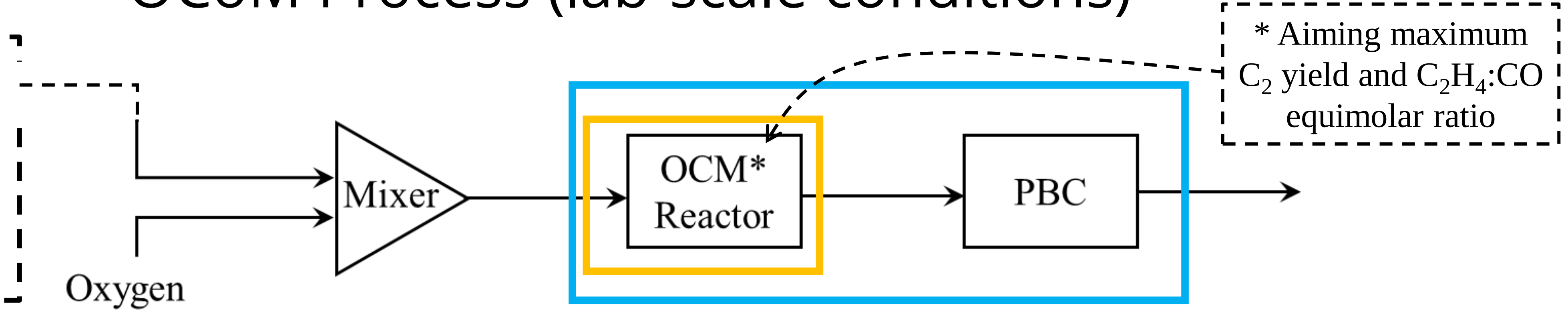
OCoM Process (lab-scale conditions)

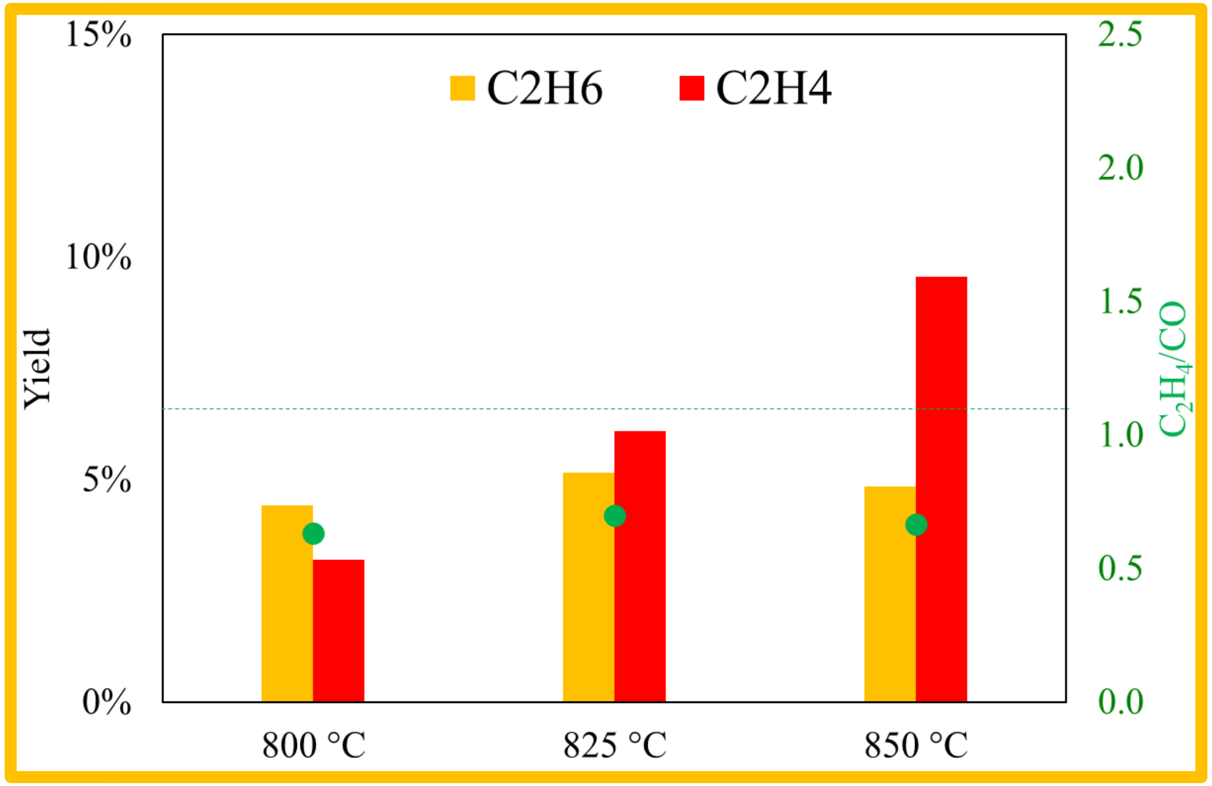
T = 800 – 850 °C

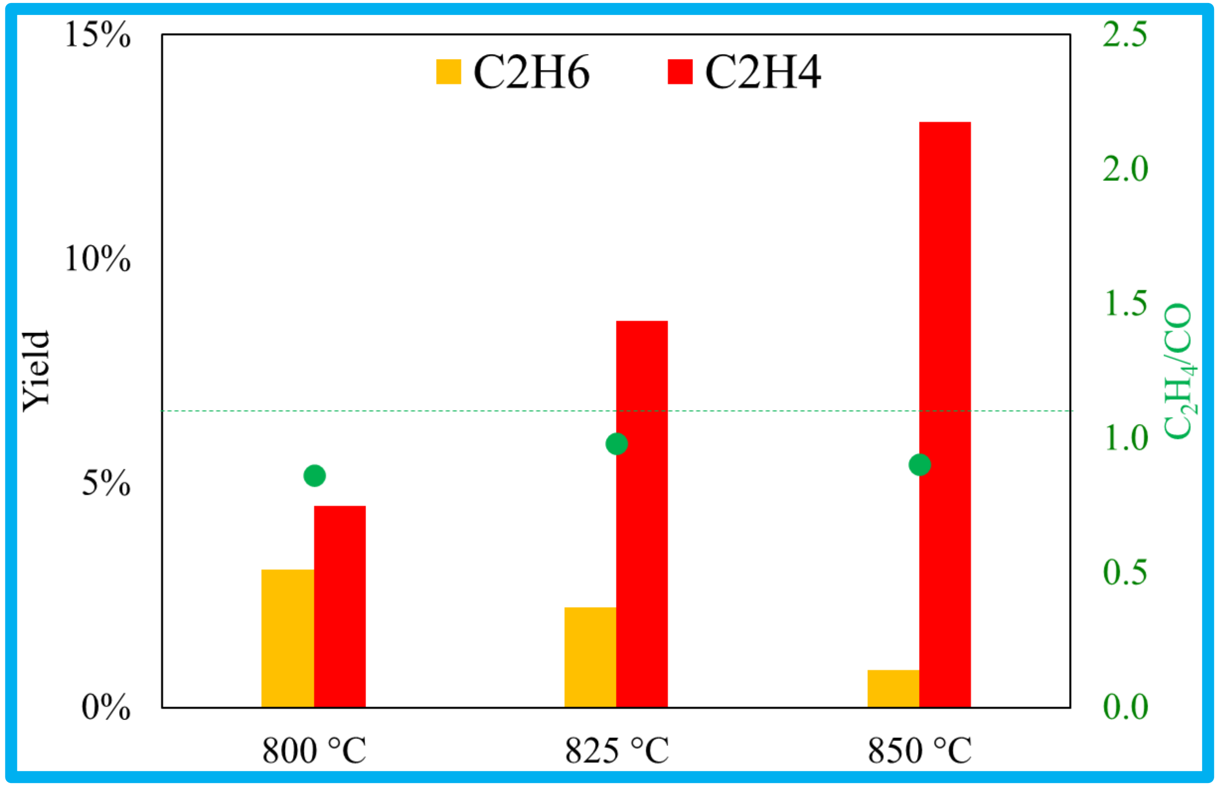
p_T = 1 bar;

CH_4/O_2 = 4

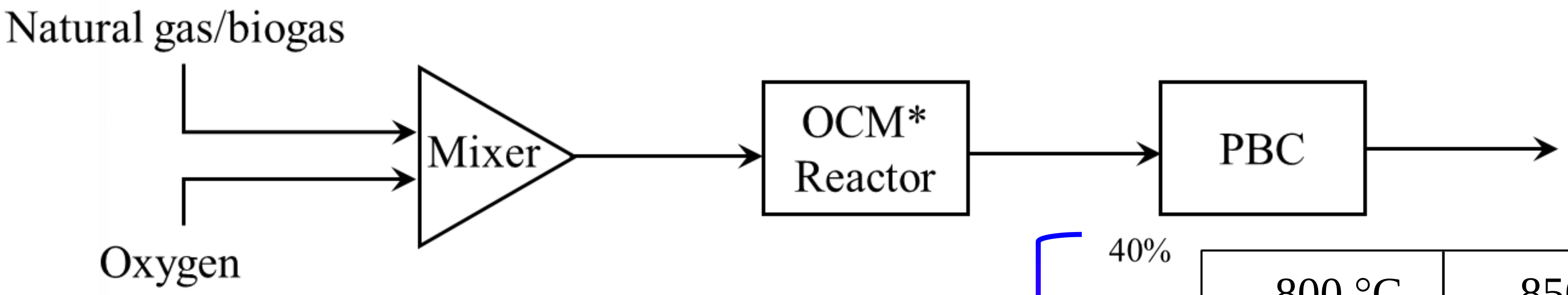
W/F_{CH4} = 2.5 kg s mol^{-1}





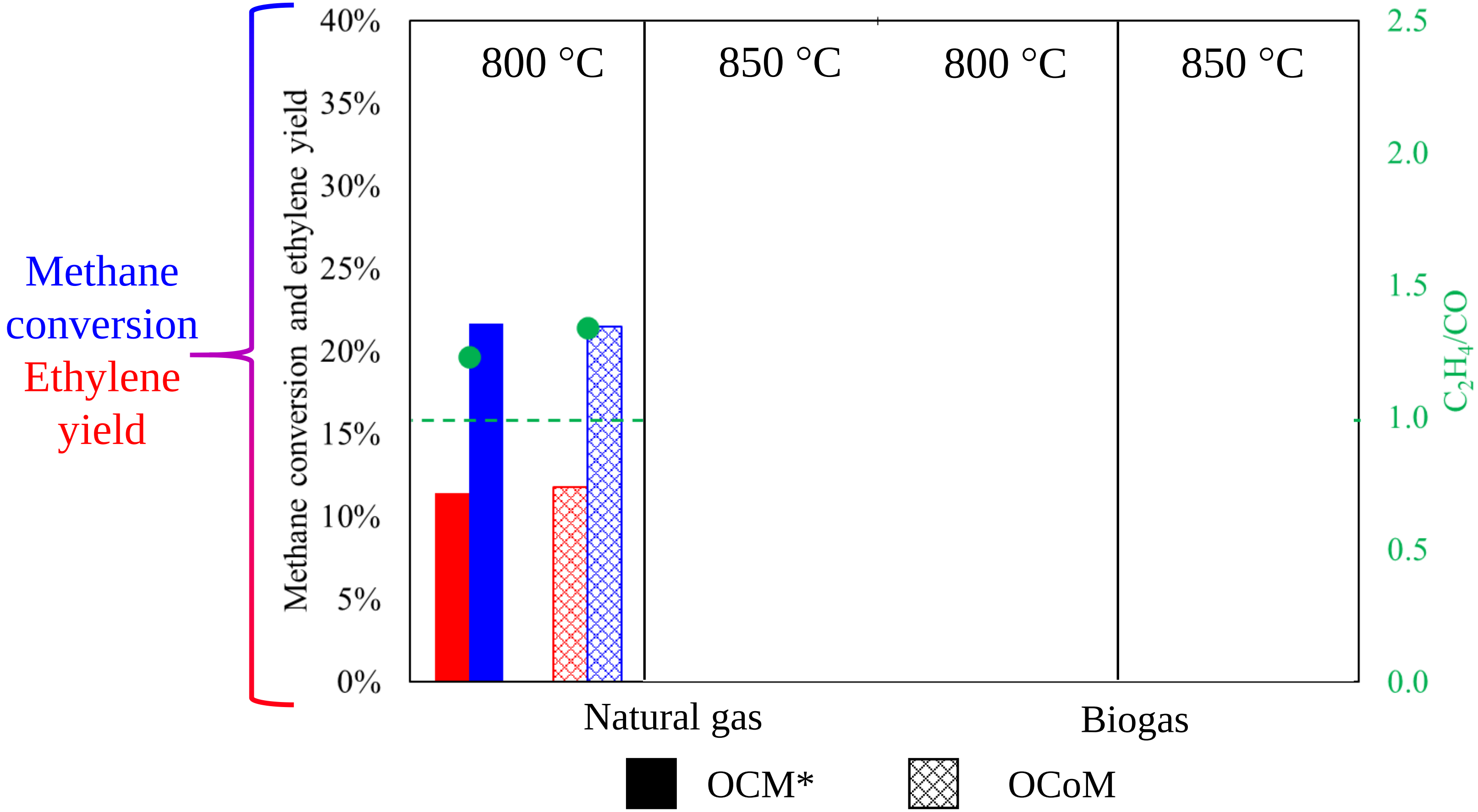


OCoM – Real scenarios (Natural gas and Biogas)



Approximation of the compositions of natural gas and biogas		
	Composition (mol%)	
Component	Natural gas	Biogas
Methane	82.43	63.45
Ethane	7.76	0
Propane	2.86	0
CO_2	6.95	36.55

$CH_4/O_2 = 4$; $W_{cat}/F_{CH4} = 2.5$ kg mol^{-1} s^{-1}



Conclusions

- The $MnNaW/SiO_2$ catalyst has the highest ethylene yield, being the most suitable for OCoM.
- A simple 8 steps kinetic model for OCM was developed and incorporated into the OCoM process simulations.
- Using natural gas for OCoM results in a maximal ethylene yield of 15% with a C_2H_4/CO ratio of 1.5 at temperature of 850 °C, total pressure of 1 bar, W/F_{CH4} of 2.5 kg mol^{-1} s^{-1}, and CH_4/O_2 of 4.

Outlook

- In order to improve the simple kinetic model, more experimental data focusing on the role of the water should be acquired for further parameter re-estimation.
- Scaling-up of the catalyst (pellets synthetization)
- Incorporating of kinetic model within a packed bed reactor model in order to assess the OCoM process performance.
- Scaling-up of the process to pilot-plant and industrial-scale

THANK YOU

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